

# Cocoa Butter-Like Fats from Domestic Oils<sup>1,2</sup>

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COCOA BUTTER is a premium candy fat primarily because of its unique physical characteristics.

At room temperatures below about 26°C. it is hard and brittle, yet when eaten it melts completely in the mouth with a pleasing, cooling sensation. The solids content of a sample of cocoa butter has been estimated to be 71% at 25°C., 51% at 30°C., and only 5% at 35°C. (1, 8). The plastic range is very short when compared with that of most other fats.

The fatty acid composition of cocoa butter is not unique. According to Meara (11), the component fatty acids and their mole percentages in a sample of cocoa butter he examined were found to be as follows: oleic, 37.3; stearic, 34.4; palmitic, 26.2; and linoleic, 2.1. Others have obtained similar data. The percentages and types of fatty acids cited are similar to those occurring in the glycerides of mutton tallow.

The distinctive physical properties of cocoa butter are a reflection of an unusual glyceride composition. Unlike most fats and oils, the types of glycerides occurring in cocoa butter are small in number, and two or three of these comprise 80-85% of the total weight. Meara (11) calculated the composition for one apparently representative sample of cocoa butter to be as follows:

	Mole percentage
Fully saturated triglycerides.....	2.6
Oleodipalmitin.....	3.7
Oleopalmitostearin.....	57.0
Oleodistearin.....	22.2
Palmitodiolein.....	7.4
Stearodiolein.....	5.8
Triolein.....	1.1

The development of a good cocoa butter-like fat from domestic oils is desirable in a number of respects. Also a cocoa butter-like fat could have properties even more desirable than those of cocoa butter itself. The latter has a softening point which is slightly too low for products intended for consumption in the summer-time.

The armed forces have need for a confectionery fat similar to cocoa butter but with an appreciably higher melting point. Such a product would most logically be based on a fat mixture resembling cocoa butter but having a slightly higher melting point; that is, the main ingredient would be a fat closely resembling cocoa butter.

Any cocoa butter replacement, whether it be for general use or for the armed forces, would in most instances be used in combination with cocoa or chocolate liquor. This imposes the further restriction that the solid forms of the replacement fat and the fat in cocoa or chocolate liquor be mutually compatible; that is, one must not change the softening or melting characteristics of the other. A fat like palm kernel

stearin would not be a satisfactory replacement. Recently Steiner (12) presented data showing that the addition of one part of palm kernel stearin containing 23% of liquid at 25°C. to one part of cocoa butter sample containing about 21% of liquid at 25°C. yielded a mixture having about 46% of liquid at the same temperature. In practice the most successful cocoa butter replacement would contain largely glycerides identical with the major glycerides in cocoa butter.

The investigation which will be reported here was concerned with the preparation and examination of a number of possible cocoa butter-like fats. They were prepared by esterification or interesterification followed by fractionation. Testing consisted of determining melting points, consistency vs. temperature characteristics, and softening points of the several products and their mixtures with cocoa butter.

## Materials and Procedures

**Materials.** The oleic acid used in preparing products by way of esterification was derived from pecan oil. The latter was interesterified at 50°C. in the presence of an excess of methyl alcohol and a small amount of sodium methylate to produce the methyl esters, which were treated with acetic acid, washed with water, and distilled. The second or main fraction from the still was mixed with acetone (15 ml. per gram of esters) and crystallized at -60°C. The precipitate from this crystallization was again mixed with acetone (10 ml. per gram of esters) and crystallized at -37°C. The filtrate obtained was diluted with acetone, and a second crystallization at -60°C. was carried out. The methyl oleate, obtained as the precipitate in the final crystallization, had a purity of about 90% (14). Saponification of the methyl oleate, followed by acidulation of the soaps and washing, yielded the oleic acid.

The stearic acid was a commercial product, Hystrene S-97,<sup>4</sup> produced by the Trendex Company, and purified before use. Purification consisted of three crystallizations from acetone (3 g. of acetone per 1 g. of acid) at room temperature (25°C.).

The palmitic acid was Armour's Neo Fat 1-56,<sup>4</sup> which also was purified further before use. The palmitic acid was crystallized once from acetone, converted to the methyl ester, fractionated in a Podbielniak still,<sup>4</sup> and reconverted to the fatty acid.

The olive oil and the hydrogenated cottonseed oil (iodine value, <1) were obtained from commercial sources. Both products were further purified in the laboratory before being used. The olive oil, which was of virgin grade, was refined with caustic soda, bleached with a neutral, activated clay, and dried. The hydrogenated cottonseed oil was crystallized once from acetone to remove free fatty acids.

The samples of cocoa butter and the candy fats,

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<sup>4</sup> This product or apparatus is named as part of the exact experimental conditions. Naming it does not constitute an endorsement of the product or apparatus over that of any other manufacturer.

which contained coconut oil, were obtained from commercial sources.

**Procedures.** Esterification of the fatty acids was carried out essentially as described in an earlier article (7). Approximately 98% of the theoretical amount of glycerol required to react with the fatty acids was used, and the catalyst, which consisted of stannous chloride dihydrate, was employed in an amount of 0.00114 moles per 100 g. of fatty acids. The reaction was allowed to proceed for 2 hrs. at 200°C. while the reactants were stirred under an atmosphere of hydrogen and a pressure of 20 mm. of mercury. The crude reaction product was refined with caustic soda and bleached with neutral, activated clay in the usual manner to remove the catalyst and the excess of fatty acids. The final product contained no free fatty acids and had a hydroxyl value of practically zero.

The interesterification reaction between the olive oil and the hydrogenated cottonseed oil or tristearin was carried out under one atmosphere of hydrogen for 1 hr. at 60 to 80°C. in the presence of 0.15% of sodium ethylate. After completion of the reaction the crude product was washed with dilute acetic acid and refined with caustic soda.

To fractionate the various triglyceride products into trisaturated, monounsaturated, diunsaturated, and triunsaturated glycerides, several schemes were tried. The most effective and also the simplest scheme, which was adopted, consisted of dissolving 1 part of the reaction product in 15 or 30 parts of acetone, by weight, allowing the solution to come to room temperature (25°C.) overnight, removing the precipitate (trisaturated fraction), cooling the remaining solution to 0°C., and again removing the precipitate (monounsaturated fraction). This last was the cocoa butter substitute. In the filtrations performed in these separations the filter cake was not washed. Solvent was removed as thoroughly as possible by suction. At the completion of the operation the cake contained about an equal weight of entrapped solvent.

**Test Methods.** Three methods were used to characterize the several cocoa butter substitutes and their mixtures with cocoa butter. Capillary melting points were determined. Consistency *vs.* temperature curves were established, using a falling needle type of micro-penetrometer and technique essentially as described previously (6) except that tempering was performed at room temperature and for longer periods of time and that tests were made at three-degree intervals. Softening points or open-tube melting points were obtained by the A.O.C.S. Method Cc 3-25 except that the method of tempering was changed.

In each of the three types of tests the samples were heated to just above their melting points. Then they were cooled with stirring until crystals formed, after which they were placed in the tubes or penetrometer blocks. Tempering was carried out at a few degrees below the melting point of each sample and for periods of time varying from one day to two weeks, *i.e.*, until further tempering produced practically no change.

## Results and Discussions

**Products Prepared from Purified Fatty Acids.** Esterification of a mixture of saturated and unsaturated fatty acids with an equivalent amount of glycerol yields statistically calculatable proportions of triglycerides of various degrees of unsaturation. Figure 1 shows graphically the triglyceride composition

*vs.* the oleic acid content of a mixture of oleic and stearic acids used in an esterification reaction.

Obviously, if a cocoa butter-like fat containing mostly oleodisaturated glycerides is to be prepared by way of random esterification followed by fractionation, the fatty acid mixture to be esterified should be low in oleic acid. If the mole percentage of oleic acid in the mixed acids is sufficiently low, the proportions of di- and triunsaturated glycerides produced will be such that they may not have to be removed from the monounsaturated fraction to obtain a cocoa butter-like fat; *i.e.*, all of the unsaturated triglycerides would be used. Figure 2 shows the composition and total yield of the unsaturated triglycerides which would be obtained on esterifying a mixture of oleic and stearic acids and then removing only the trisaturated fraction.

In the products prepared from the purified oleic, stearic, and palmitic acids, which will be described below, the mole percentage of oleic acid in the fatty acid mixture always was 25. Such mixtures theoretically yield a fat of the following triglyceride composition:

	Mole percentage
Trisaturated glycerides.....	42.2
Disaturated, monounsaturated glycerides.....	42.2
Monosaturated, diunsaturated glycerides.....	14.0
Triunsaturated glycerides.....	1.6

Data on the fractions actually obtained on crystallization of the esterification products from acetone by the method mentioned in the section on procedure are recorded in Table I.

Two fractionation runs were made with each product to obtain a check on the yields. The weight percentages of the trisaturated and monounsaturated fractions listed in Table I are uncorrected; that is, no corrections were made for the minor amounts of glycerides dissolved in the acetone remaining in the filter cake when the fractions were obtained.

Calculations show that the trisaturated fractions listed in Table I contain nearly all of the trisaturated glycerides. For example, by correcting the experimental value for trisaturates in Fractionation No. 1-7 (Table I) on the assumption that the iodine value is a reflection of the content of disaturates, a corrected value of 42.0 is obtained. The excellent agreement with the theoretical value of 41.9 is somewhat fortuitous inasmuch as the oleic acid used in the prepara-

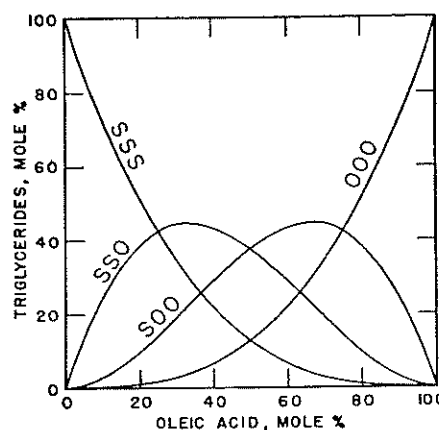


FIG. 1. Theoretical yield of tristearin (SSS), oleodistearin (SSO), steardiolein (SOO), and triolein (OOO) *vs.* oleic acid in the oleic and stearic acid mixture esterified with an equivalent amount of glycerol.

TABLE I  
Yields of the Fractions Obtained on Crystallization of Esterified Products from Acetone

Fractionation No.	Component acids of esterified product	Iodine value of product	Yield and iodine value of fractions obtained on crystallization from acetone					
			Trisaturated		Monounsaturated <sup>a</sup>			Di- and triunsaturated
			Wt. %	I.V.	Fraction No.	Wt. %	I.V.	Wt. %
1-4	Stearic 42 Palmitic 33 Oleic 25	19.8	47.6	—	1-4C	37.2	26.7	15.2
1-5	Same as 1-4	—	48.5	3.6	1-5C	33.3	28.4	18.2
1-7	Same as 1-4	—	47.7	3.5	1-7C	36.9	27.5	15.8 <sup>b</sup>
2-1	Palmitic 75 Oleic 25	20.4	48.0	—	2-1C	28.1	—	23.9
2-2	Same as 2-1	—	50.8	4.5	2-2C	27.4	29.0	21.8
3-1	Stearic 75 Oleic 25	19.1	53.1	—	3-1C	31.1	—	15.8
3-2	Same as 3-1	—	55.2	3.9	3-2C	35.2	29.5	9.6
7-1	Cocoa butter, A	37.8	0	—	7C	74	—	26

<sup>a</sup> Cocoa butter-like fraction of esterified product.

<sup>b</sup> Iodine value of this fraction was 48.9.

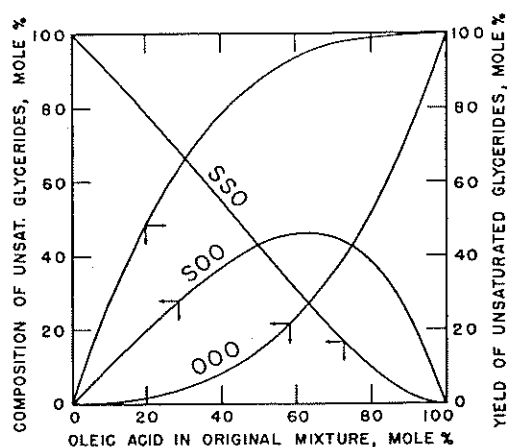


Fig. 2. Theoretical yield and composition of the unsaturated triglycerides obtained on esterifying mixtures of oleic and stearic acids. SSO, SOO, and OOO represent oleodistearin, steardo-olein, and triolein, respectively. Dotted line indicates yield of unsaturated triglycerides.

tion contained a small amount of saturated component.

Data published by other investigators on the solubility of saturated triglycerides also leads one to expect that tristearin and palmitostearins would be quite insoluble in acetone at room temperature even if the acetone contained small amounts of other fats. Chen and Daubert (3) found, for example, that laurylmyristostearin was soluble to the extent of only 0.18 g. in 100 g. of acetone at 25°C.

The monounsaturated or cocoa butter-like fractions listed in Table I apparently were quite free of di- and triunsaturated glycerides. Yield data and iodine values for these fractions coupled with the knowledge that these fractions could not contain appreciable amounts of trisaturated glycerides leads to this conclusion. The behavior of cocoa butter, when fractionated under identical conditions (see Table I), lends further support to the conclusion.

One of the requirements of a satisfactory cocoa butter-like fat is that it not change significantly the melting characteristics of cocoa butter with which it may be admixed. In this connection it should be recalled that invariably the melting point of a pure glyceride or fat mixture is depressed by the addition of a small amount of a different glyceride or fat mixture. The amount of depression which is attained depends upon the amount and nature of added com-

ponent. The maximum amount of depression for glycerides generally ranges between a fraction of a degree and several degrees centigrade (2).

Several of the monounsaturated (cocoa butter-like) fractions listed in Table I were mixed with cocoa butter, portions of the mixtures were tempered in capillary tubes, and melting characteristics were determined. For comparison, similar mixtures with cocoa butter were made with two commercial candy fats, a completely hydrogenated coconut oil, and a fraction from cocoa butter. The results obtained are recorded in Table II.

Cocoa Butter Fraction 7C (Table I) was quite compatible with cocoa butter. The 1:1 mixture started to melt and melted almost completely at temperatures about midway between those for the two components. Fraction 1-5C, consisting essentially of mixed oleo-palmitostearins, was about as compatible as was Fraction 7C. The next most compatible fractions were 3-2C and 2-2C, in the order mentioned. The commercial candy fats A and B, which contained coconut oil, and the hydrogenated coconut oil were least compatible.

Another requirement of a good cocoa butter replacement is that it and its mixtures with cocoa

TABLE II  
Melting Characteristics of the Cocoa Butter-Like Fractions, Cocoa Butters, and Their Mixtures <sup>a</sup>

Fraction or mixture	Melting first noticed	Mostly melted (75-90%)	Nearly all melted (96%)
	°C.	°C.	°C.
Fraction No. 1-5C.....	36.0	37.8	39.5
Mixture.....	32.7	34.9	35.7
Cocoa butter B.....	31.3	33.8	34.9
Fraction No. 2-2C.....	37.8	42.7	44.8
Mixture.....	31.5	33.0	35.2
Cocoa butter B.....	31.3	33.8	34.9
Fraction No. 3-2C.....	37.6	40.8	42.7
Mixture.....	35.2	37.6	38.7
Cocoa butter B.....	31.3	33.8	34.9
Candy fat A.....	32.0	39.5	43.1
Mixture.....	< 23.4	32.0	32.8
Cocoa butter B.....	31.3	33.8	34.9
Candy fat B.....	32.0	37.8	39.5
Mixture.....	< 23.4	29.4	30.3
Cocoa butter B.....	31.3	33.8	34.9
Completely hydrogenated coconut oil.....	< 23.4	28.9	30.3
Mixture.....	< 23.4	< 23.4	< 23.4
Cocoa butter B.....	31.3	33.8	34.9
Fraction 7C from cocoa butter A.....	32.6	33.9	35.0
Mixture.....	32.4	32.6	33.6
Cocoa butter A.....	30.8	32.6	33.6

<sup>a</sup> All mixtures are 1:1 by weight.

butter soften and melt over a short temperature interval; *i.e.*, the product and its mixtures must have an extremely short plastic range. That the cocoa butter-like fractions represented in Table I meet these requirements is indicated in the consistency *vs.* temperature curves of Figure 3. All of the fractions and mixtures tested yielded curves closely resembling that of cocoa butter.

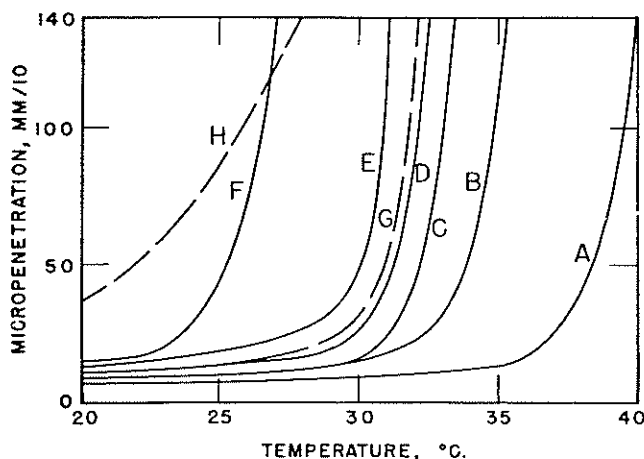


Fig. 3. Consistency curves: *A*, oleodistearin fraction (3-2C); *B*, oleopalmitostearin fraction (1-5C); *C*, oleodipalmitin fraction (2-2C); *D*, 1:1 mixture of cocoa butter *B* and oleodistearin fraction (3-2C); *E*, 1:1 mixture of cocoa butter *B* and oleopalmitostearin fraction (1-5C); *F*, 1:1 mixture of cocoa butter *B* and oleodipalmitin fraction (2-2C); *G*, cocoa butter *B*; and *H*, all hydrogenated cottonseed oil, iodine value 65.5.

Open-tube melting points (softening points) were determined for a series of mixtures of cocoa butter and each of the cocoa butter-like fractions, Cocoa Butter Fraction 7C, and Candy Fat A (washed). The results obtained are recorded in Figure 4. As is evident from the curves, the first addition of the cocoa butter-like fractions to cocoa butter caused a depression of the softening points; but when enough of each fraction had been added to produce 1:1 mixtures, the softening points were between those of the separate components. Of the three fractions the oleopalmitostearin fraction (1-5C) caused the least amount of depression while the oleodipalmitin fraction (2-2C) caused the greatest amount. The order of compatibility shown here is in accord with the relative amounts of these types of glycerides in cocoa butter. The Cocoa Butter Fraction 7C, when mixed with cocoa butter, produced no measurable depression of the softening point. The mixtures of Candy Fat A yielded a curve indicating good compatibility; however the character of these mixtures differed markedly from that of the other mixtures tested.

In preliminary tests with mixtures of Candy Fat A and cocoa butter the mixtures appeared to melt before the pressure of the water on the open end of the capillary tube caused them to flow. Consequently the softening points obtained were believed to be higher than justified. Because the candy fat contained lecithin, the fat was washed with water to remove the lecithin and then dried. The data obtained with this fat are recorded as Curve *E*, Figure 4. The water washing changed the shape of the curve slightly and raised the melting point of the fat, but the fat still melted to a large extent before it moved in the capillary tube.

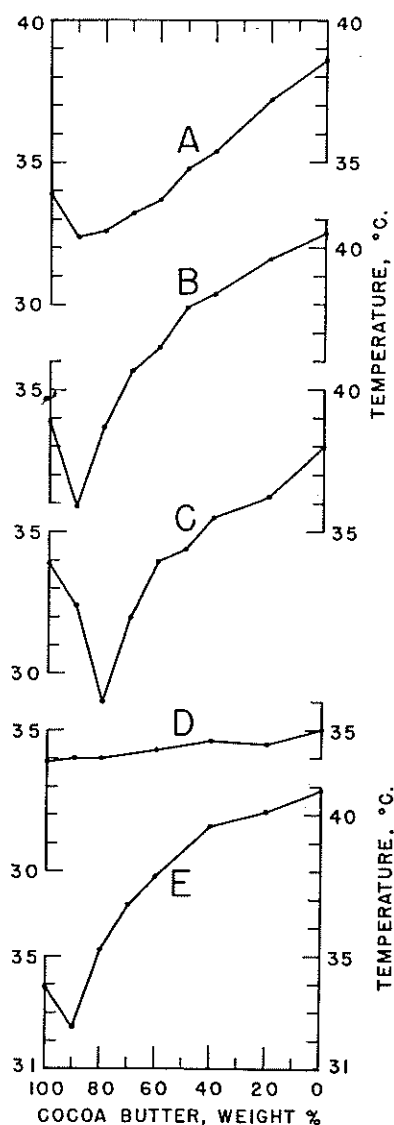


Fig. 4. Softening point of mixtures of cocoa butter *A* with *A*, oleopalmitostearin fraction (1-5C); *B*, oleodistearin fraction (3-2C); *C*, oleodipalmitin fraction (2-2C); *D*, cocoa butter fraction (7C); and *E*, candy fat *A* after washing.

On the basis of the several tests performed, the monounsaturated glyceride fractions represented in Table I are not entirely compatible with cocoa butter; the oleodipalmitin fraction (2-2C) is the least compatible. The probable cause of the incompatibility is the presence in the fractions of certain isomers not found in cocoa butter. The conclusion regarding compatibility conforms with a claim by Verkade (13) that, on mixing the oleopalmitostearins in pairs, clear melting-point depressions are encountered. Nevertheless it would appear that the isomers within each group are so alike in structure and have almost the same melting points (10, 4, 5) that at least the oleopalmitostearins and the oleodistearins should in practice make good cocoa butter substitutes. The addition of one or two glycerides closely related to cocoa butter might even improve certain characteristics desired in this product.

*Practical Preparation of a Cocoa Butter Substitute.* The large scale preparation of cocoa butter-like fats from purified fatty acids might be economically feasible, but there are available more attractive methods

of preparation. One of these involves the interesterification of a completely hydrogenated fat and a natural oil whose component fatty acids are rich in oleic and the subsequent fractionation of the reaction product. The unwanted fraction or fractions would be recombined in subsequent interesterifications. Completely hydrogenated cottonseed oil, whose glycerides contain approximately 75% stearic and 25% palmitic acid by weight, should be suitable as one of the starting materials. For the source of oleic acid, domestic olive oil would be the best material commercially available. Its component acids and their weight proportions (9) are approximately as follows: oleic, 85%; linoleic, 5%; palmitic, 7%; and stearic, 3%.

In the current investigation a cocoa butter-like fat was prepared by interesterifying 70 parts by weight of completely hydrogenated cottonseed oil with 30 parts by weight of domestic olive oil. After the reaction product was purified, it was fractionated by crystallization from acetone by the usual procedure except that the weight ratio of acetone to product employed was 15:1. The yield of the trisaturated fraction filtered from the acetone solution at 25°C. was 39.6%. A portion of the filtrate obtained at 25°C. was stripped to recover a fraction, 4-1B, which had an iodine value of 39.3 and was composed of practically all of the unsaturated glycerides in the interesterification product. The yield of fraction 4-1B was 60.4%, after correction for the weight of filtrate not stripped.

The bulk of the filtrate obtained at 25°C. was cooled to 0°C., and the fraction containing the mono-unsaturated glycerides was collected by filtration. This fraction, 4-1C, iodine value 29.3, was obtained in a yield of 29.3%, after correction for the weight of filtrate removed at 25°C.

Consistency vs. temperature curves for fractions 4-1B and 4-1C are recorded in Figure 5. Also shown in the figure are curves for a typical cocoa butter and an all-hydrogenated cottonseed oil, iodine value 58.6. The latter product is about comparable in consistency to some candy fats currently being marketed.

According to the consistency curves, Fraction 4-1C has a softening range which is somewhat longer than that for cocoa butter but not nearly as long as that for the all-hydrogenated cottonseed oil. In confections the Fraction 4-1C might be a good replacement for cocoa butter.

In preliminary tests, chocolate bars were prepared which contained 21.9% of Fraction 4-1C and 17.9% of chocolate liquor; these two components were the only fatty materials in the formulation. No difficulties were encountered in the molding or handling of the bars. The eating qualities were considered to be very good. When the bars were heated to 100°F., kept at this temperature, and cooled back to room temperature, there was no evidence of fat bloom.

### Summary

Technical considerations indicate that cocoa butter-like mixtures can be prepared readily by the esterification of mixtures of oleic, palmitic, and stearic

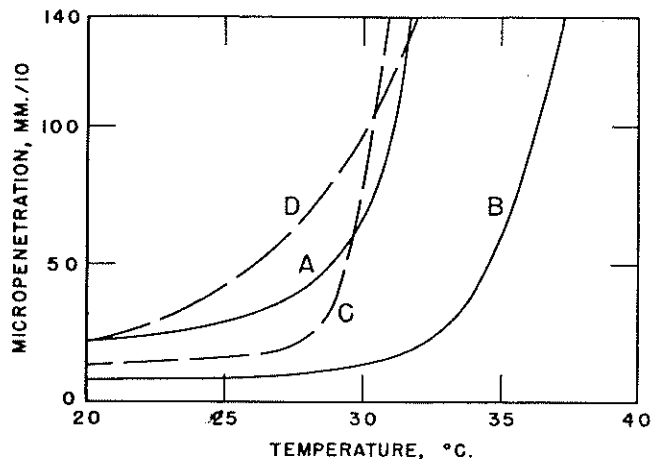


Fig. 5. Consistency curves: A, unsaturated fraction (4-1B) from interesterified olive oil and hydrogenated cottonseed oil; B, monounsaturated fraction (4-1C) from olive oil and hydrogenated cottonseed oil; C, a typical cocoa butter; and D, all hydrogenated cottonseed oil iodine value 58.6.

acids, or the interesterification of their glycerides, followed by the fractional crystallization of the reaction products.

Using the indicated procedures, three cocoa butter-like fractions were prepared. One consisted essentially of oleopalmitostearins, another consisted essentially of oleodistearins, while the third consisted mostly of oleodipalmitins.

On the basis of softening point curves, the oleopalmitostearin product was most compatible with cocoa butter, the oleodistearin product was the next most compatible, while the oleodipalmitin product was least compatible. When mixed with cocoa butter, all three of the products produced consistency vs. temperature curves whose shapes closely resembled that of cocoa butter. All of the mixtures softened over a short temperature interval though the actual temperature at which softening occurred varied. The several products are believed to be satisfactory cocoa butter replacements.

Another cocoa butter-like fat was prepared by the interesterification of 70 parts of completely hydrogenated cottonseed oil and 30 parts of olive oil and the subsequent fractionation of the reaction product.

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